

# Identification of a Triplet-Pair Intermediate in Singlet Exciton Fission in Solution

Hannah L. Stern<sup>1</sup>, Andrew J. Musser<sup>1</sup>, Simon Gelinás<sup>1</sup>, Patrick Parkinson<sup>2</sup>, Laura Herz<sup>2</sup>, Matthew J. Bruzek<sup>3</sup>, John Anthony<sup>3</sup>, Richard H. Friend<sup>1</sup> and Brian J. Walker<sup>1</sup>

<sup>1</sup> Cavendish Laboratory, University of Cambridge, J.J Thompson Avenue, CB30HE, UK <sup>2</sup> Clarendon Laboratory, Parks Road, University of Oxford, Oxford, OX13PU, UK <sup>3</sup> Department of Chemistry, University of Kentucky, Lexington, Kentucky, KY40506, USA

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**Singlet exciton fission is the spin-conserving transformation of one spin-singlet exciton into two spin-triplet excitons. This exciton multiplication mechanism offers an attractive route to solar cells that circumvent the single-junction Shockley-Queisser limit. Most theoretical descriptions of singlet fission invoke an intermediate state of a pair of spin-triplet excitons coupled into an overall spin-singlet configuration, but such a state has never been optically observed. In solution, we show that the dynamics of fission are diffusion limited and enable the isolation of an intermediate species. In concentrated solutions of bis(triisopropylsilyethyl)nyl (TIPS)-tetracene we find rapid (<100 ps) formation of excimers and a slower (~10 ns) break-up of the excimer to two triplet exciton-bearing free molecules. These excimers are spectroscopically distinct from singlet and triplet excitons, yet possess both singlet and triplet characteristics, enabling identification as a triplet-pair state. We find that this triplet-pair state is significantly stabilised relative to free triplet excitons, and that it plays a critical role in the efficient endothermic singlet fission process.**

singlet fission | photochemistry | TIPS-tetracene

## Introduction

The fission of photogenerated spin-singlet excitons into pairs of spin-triplet excitons is an effective way to generate triplet excitons in organic materials [1][2]. Because the triplets produced are coupled into an overall singlet state, spin is conserved and triplet formation can proceed on sub-100 fs timescales [1][3][4][5] with yields of up to 200% [1][6][7]. Current interest in singlet fission is driven by its potential to improve the efficiency of solar cells by circumventing the Shockley-Queisser limit for single-junction devices [8][9][10]. Incorporating a singlet-fission material within a low-band-gap solar cell, it should be possible to capture the energy normally lost to thermalisation following the absorption of high-energy photons [11][12]. An external quantum efficiency of 129% [13] and an internal quantum efficiency of >180% [14] have been reported using pentacene as the singlet fission material and fullerene (C<sub>60</sub>) as electron acceptor. In spite of such significant advances, many questions remain about the underlying mechanism of triplet formation, such as the role of intermediate electronic states and the ability of systems to undergo endothermic fission.

The basis of most kinetic descriptions of singlet fission is the triplet-pair state <sup>1</sup>(TT), which is entangled into an overall singlet and is an essential intermediate for the formation of two free triplet excitons [1][15]. Whether this intermediate state is present only transiently, as expected in exothermic systems such as pentacene, or whether it can be sufficiently long-lived to also play a central role in the fission process in slower systems is unclear. Transient absorption measurements of the canonical systems pentacene and tetracene in the solid state allow clear identification of only the singlet and triplet states [3][6][16][17] meaning the character of any intermediate has not been observed directly. Other factors affect fission in the solid state that can complicate analysis, such as exciton diffusion, delocalisation of excitations and the heterogeneity of materials.

Singlet fission in solution offers an alternative approach to investigate the intermolecular interactions that mediate fission. The conformational freedom of molecules and diffusional timescales enable a new approach to investigating fission in systems where the essential photophysics, such as the progression of excited states and relative zero-point energies, are not expected to differ largely from the solid state. Some of the authors have recently demonstrated that quantitative singlet exciton fission can be achieved in TIPS-pentacene when a molecule with a singlet exciton collides with a molecule in its ground state through diffusion, with triplet yields reaching 200% at high concentrations [18]. Whilst the triplet yields are comparable to the solid state, fission proceeds orders of magnitude more slowly in solution, offering a clearer picture of the evolution of the states involved. These results pointed to excimer formation as the driving force enabling singlet fission, but this state was too short-lived for a clear identification.

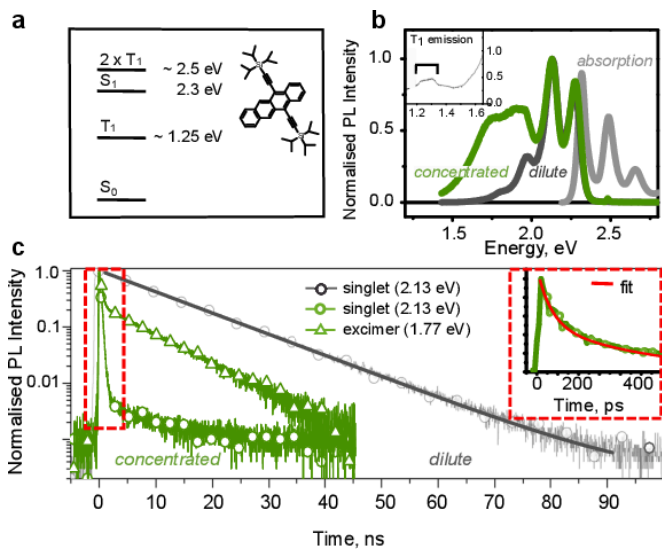
To resolve the role of such intermediates in solution-based singlet fission, we draw on the well-established study of pentacene and tetracene in the solid state. Whereas singlet fission in pentacene is exothermic by ~100 meV [1], in tetracene it is found to be endothermic by ~180 meV [1][19][20][21]. Accordingly, triplet formation is significantly faster in pentacene films (~80 fs)[5] than in tetracene (~90 ps) [22], though curiously in the latter material the process remains highly efficient and fully independent of temperature [22][23]. In this study, we study solutions of TIPS-tetracene, a tetracene derivative also capable of singlet fission [24]. Analogous to tetracene films, we determine that TIPS-

## Significance

**We use transient spectroscopy to investigate the mechanism of singlet exciton fission, a quantum mechanical phenomenon in some organic molecules in which a spin-singlet excited state can split into two spin-triplet states. This process may be harnessed to boost solar cell efficiencies, but the underlying mechanism remains poorly understood. Central to most models is a triplet-pair state, consisting of two triplets entangled into an overall spin-singlet configuration, but it has never before been optically detected. In a solution-based system, we detect a state with simultaneous singlet- and triplet-exciton character which dissociates to form triplet excitons in 120% yield. We consider that this intermediate constitutes a triplet-pair state, and its observation allows important insight into the nature of triplet exciton coupling.**

## Reserved for Publication Footnotes

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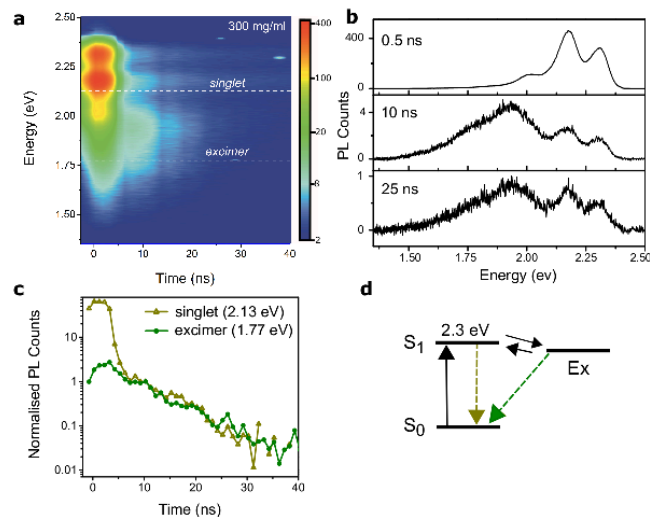


**Fig. 1. The absorption and emission spectra of TIPS-tetracene show excimer formation in concentrated solutions.** (a) The excited state energy diagram and chemical structure of TIPS-tetracene. The triplet energy was obtained from the phosphorescence observed in a film of dilute TIPS-tetracene and polystyrene (inset Figure 1b). (b) UV-Vis absorption (light grey) of 0.3 mg/ml TIPS-tetracene in  $\text{CHCl}_3$ . UV-Vis spectra were recorded for solutions from 0.03-300 mg/ml and no change was observed in the absorption peak positions (Fig. S3). The normalized steady-state photoluminescence spectra of 300 mg/ml (dark green) and 3 mg/ml (dark grey) show that excimeric emission, centered at 1.75 eV, in the concentrated solution is absent in the dilute solution. The phosphorescence observed in a film in the inset [36]. Interference at 1.2 eV, from the excitation source, has been removed for clarity. (c) The normalized time-resolved photoluminescence decay of the dilute solution at the 'excitonic' (2.13 eV) region and the 'excitonic' and 'excimer' (1.77 eV) regions for the concentrated solution. In the dilute case (grey) the time constant of the excitonic decay is 11.6 ns and this is shortened to 140 ps in 300 mg/ml, shown in the inset. The <600 ps decay at 2.13 eV was measured using PL up-conversion with a time resolution of 200 fs. The excimeric emission of 300 mg/ml decays with two time constants; < 300 ps and 8.7 ns.

tetracene is also an endothermic singlet fission system, however here the combination of the energetics, dynamics in solution and sharply resolved spectral features allow the intermediate state to be isolated.

The absorption and emission energies in solutions of TIPS-tetracene gives a singlet exciton energy of 2.3 eV (Figure 1). No phosphorescence could be detected in solution, but in films of dilute TIPS-tetracene in a polystyrene matrix we detect weak phosphorescence centred at  $\sim 1.25$  eV at room temperature (inset Figure 1b). This is consistent with what has been measured for tetracene (1.35 eV), using the same method [36]. The endothermicity of fission in TIPS-tetracene is thus on the order of 100-300 meV, comparable to that observed in tetracene films, and films of TIPS-tetracene at room temperature display a similarly slow ( $10^3$  of ps) rate of fission as tetracene with no distinct intermediate species (SI Appendix, Figure S5).

In solution however, using transient absorption and time-resolved photoluminescence spectroscopy, we directly monitor the conversion of photogenerated singlet excitons into an excimer in <100 ps. The excimer subsequently dissociates into free triplets over 10s of nanoseconds, with a final triplet yield of 120%. We observe that the excimer carries absorption signatures of both a singlet- and triplet-character state as soon as it is formed. The rapid formation of this intermediate with spin-triplet absorption signature and emissive singlet character indicates that it is a bound state of two spin-triplet excitons. We consider that one triplet is localised on each molecule and that they are coupled into an overall spin-zero state, such that these results constitute a



**Fig. 2. The time-resolved photoluminescence of the concentrated sample indicates the singlet and excimer states are close in energy** (a) The time and spectrally resolved photoluminescence of 300 mg/ml TIPS-tetracene measured with an intensified CCD camera. (b) Timeslices at three time points in measurement (a): At 0.5 ns we observe strong singlet emission. At 10 ns and 25 ns this has decayed to show weak excimeric and singlet emission. (c), The normalized kinetics of the excimeric and singlet decay. The kinetics are normalized at 6 ns, by which time the photogenerated singlet population has fully decayed and only trace singlet emission is detected. The decay of the excimeric emission and trace singlet emission are well matched, indicating they are populated by the same excited state species, as shown schematically in the inset. (d) Schematic showing the relationship of the singlet and excimer states. Solid arrows represent absorption of light and population transfer between the two states whilst dashed lines indicate weak radiative decay.

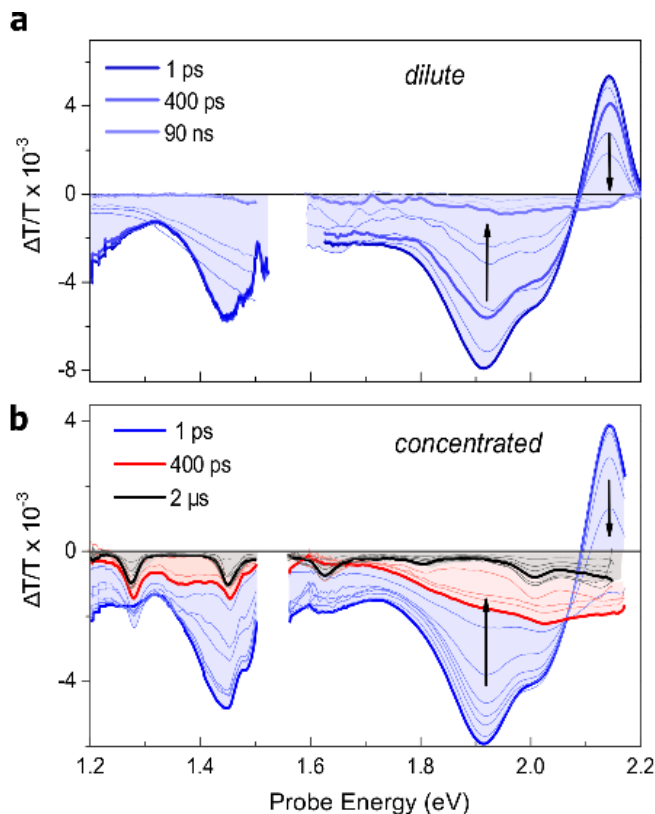
direct optical observation of a  $^1(\text{TT})$  state. In this solution system, the non-endothermic formation of this stabilised, multi-exciton excimer intermediate reduces radiative decay from the singlet and enables thermal dissociation into two free triplet excitons, with an overall energy higher than that of the original singlet exciton, in high yield.

## Results and Discussion

### Formation of Excimers

In Figure 1b we present the absorption spectrum of TIPS-tetracene in 0.3 mg/ml solution and the normalized steady-state photoluminescence spectra of both 3 mg/ml ('dilute') and 300 mg/ml ('concentrated') solutions in chloroform. We measured the UV-Vis absorption of solutions over several orders of magnitude in concentration and whilst the highest optical densities caused saturation of the detector, we observed no change in the absorption edge, lineshape or any other signs of ground-state aggregation (SI Appendix, Fig. S3). In an additional measurement, we used diffusion-ordered nuclear magnetic spectroscopy (DOSY) to determine the diffusion constant of the TIPS-tetracene molecules in the same solutions. Though the highest concentrations result in a clear increase in viscosity, this effect is of comparable magnitude for the  $\text{CHCl}_3$  molecules and TIPS-tetracene (SI Appendix, Fig. S1). These measurements provide strong evidence that over the entire concentration range the solutions contain only free, unaggregated TIPS-tetracene molecules in the ground state. In this situation, TIPS-tetracene follows the same molecular motion picture established for the solution-mediated fission in TIPS-pentacene [18]. We note, however, that the principal new finding in the present paper (of the formation of a triplet pair intermediate state, discussed below) obtains also in the presence of some molecular pre-organization. The concentration-dependent photoluminescence spectra reveal

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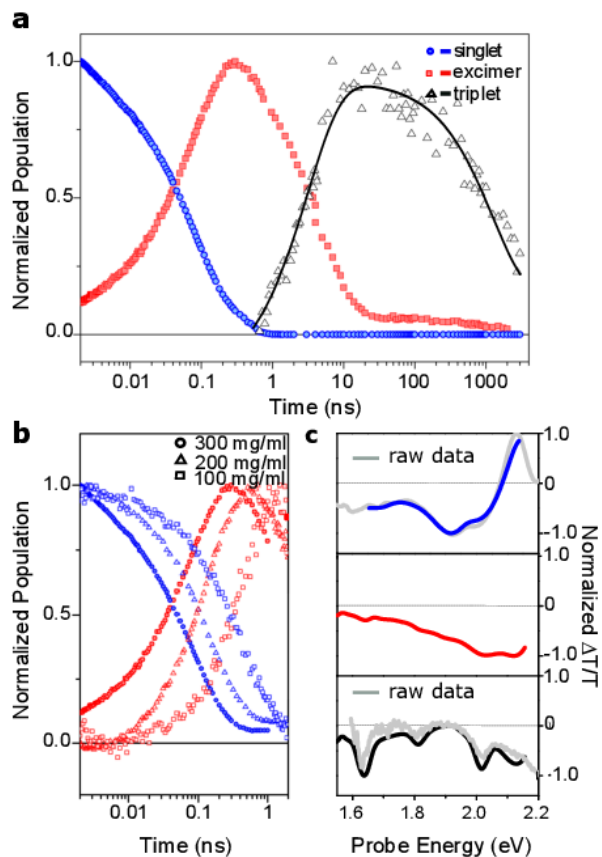


**Fig. 3. Transient absorption spectra of dilute and concentrated solutions show excimer and triplet species in the concentrated solution.** (a) Transient absorption spectra of 3 mg/ml TIPS-tetracene recorded at pump-probe time delays of 1 ps - 3  $\mu$ s. The positive feature at 2.17 eV is assigned to stimulated emission of singlet excitons and decays with the same time constant as the negative photo induced absorption feature centered at 1.9 eV (Fig. S15). (b) Transient absorption spectra of 300 mg/ml TIPS-tetracene recorded over a similar pump-probe delay range (1 ps - 3  $\mu$ s). In this measurement we observe the quenching of the initial species (blue trace) to form an intermediate by 400 ps (red trace), which decays to form triplet excitons. The triplet exciton absorption spectrum was confirmed from a separate sensitization experiment (Fig. S18). All spectra have been normalised for fluence between the NIR and visible regions. Time-slices from the ns measurement are normalised to show the triplet features.

excimer character in the excited state: we observe a broad, low-energy emissive band at high concentrations, similar to the excimer identified in TIPS-pentacene solutions.

Time-resolved photoluminescence decay of the dilute and concentrated solutions is shown in Figure 1c. In the dilute regime, the decay of the photoluminescence is mono-exponential across the emissive bandwidth and has a time constant of 11.6 ns. The emission at the 0-1 emissive peak in the concentrated solution is also mono-exponential, but is heavily quenched to 140 ps (inset Figure 1c). In accordance with this quenching, the photoluminescence quantum yield drops from 75% in the dilute solution to 2% in the concentrated. The singlet is not quenched into a completely dark state, but forms a new weakly emissive species with a featureless, red-shifted emission spectrum. Seen only in concentrated solutions, this species decays with a lifetime of 8.7 ns and is assigned to an excimer. From these photoluminescence results of the concentrated solution we can confirm the presence of two distinct emissive species that possess significantly different radiative lifetimes.

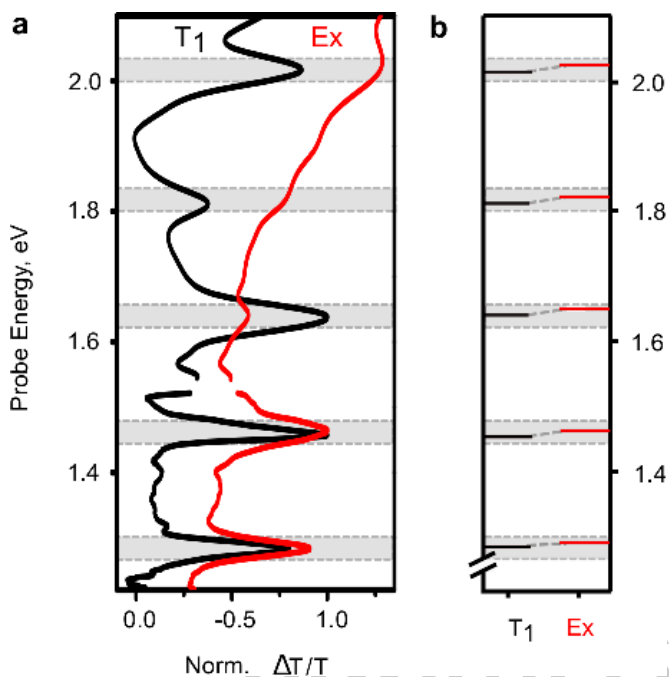
To gain a better understanding of the long-time decay kinetics, we recorded the time- and spectrally-resolved photoluminescence of the concentrated solution with an intensified CCD



**Fig. 4. The evolution of three spectral species in concentrated solution, identified by the genetic algorithm.** (a) The normalized excited state population from 100 fs (the peak of the instrument response) to 3  $\mu$ s after excitation, obtained from transient absorption measurements. The decay and rise of the singlet (blue), excimer (red) populations and the rise of the triplet (black) were obtained from sub-picosecond transient absorption, while the decay of the excimer and the decay of the triplet population were measured with nanosecond transient absorption. A guide to the eye is fitted to the triplet kinetic to show the dynamics with more clarity. (b) The corresponding singlet (blue) and excimer (red) kinetics for a range of concentrations (100-300 mg/ml). (c) Spectra of the singlet (top), excimer (middle) and triplet (bottom) obtained from genetic algorithm analysis, alongside raw TA spectra (grey) from independent reference measurements (dilute solution and sensitization).

camera (Figure 2a and 2b). In this more sensitive measurement we detect a weak long-lived component to the singlet emission decay with the same time constant as the excimeric emission (8.7 ns, Figure 2c). This observation indicates that the singlet can be re-populated by a state that is close in energy and that also gives rise to weak excimeric emission, as depicted in Figure 2d. These decay kinetics also enable us to determine the photoluminescence quantum yield of the individual components. Using spectral deconvolution methods (described below and in the SI Appendix) we can separate the PL into contributions from the prompt singlet, excimer and delayed singlet species. The delayed singlet corresponds to singlet emission after 6 ns, when we observe the onset of delayed emission kinetics (Figure 2c). Integration of the PL associated with each component gives us their contribution to the PLQE of the solution. The photogenerated singlet emission exhibits a yield of 1.3%, while the re-formed singlet and excimer emission have efficiencies of 0.3% and 0.4%, respectively. Given the low likelihood of a singlet exciton to emit before forming an excimer, we determine that 98% of the re-formed singlets





**Fig. 5.** The transient absorption spectra reveal the shift in absorption peak energies between the excimer intermediate and free triplet excitons. (a) The normalized excimer and triplet absorption spectra with the common absorption bands highlighted.

return to the excimer manifold, meaning singlet re-formation and emission are both minor decay pathways from the excimer state. The most important insight we take from this measurement is that the singlet and excimer states are close in energy.

#### Diffusional singlet exciton fission

Because the bulk of the excitations generated do not emit from either the singlet or emissive excimer states, we turn to transient absorption spectroscopy to track the evolution of these states. This pump-probe technique is widely used to study the photophysics of organic materials and is well suited to studies of singlet fission due to its ability to provide detailed signatures of emissive and 'dark' excited state species. In brief, transient absorption measures the time evolution of the absorption of a material following photoexcitation. A 'pump' pulse excites the sample, and a broad-band 'probe' pulse then arrives at a series of time delays. The transmission of the probe is measured with and without the pump, and this differential signal is normalised by the total transmission ( $\Delta T/T$ ). The result is a 2D matrix of transmission intensity as a function of time and probe energy, in which the absorption of photoexcited states is negative and photoemission stimulated by the probe is positive.

Figure 3a shows the transient absorption spectra of dilute TIPS-tetracene in chloroform, recorded over a pump-probe range of 1 ps to 3  $\mu$ s. The positive feature above 2.1 eV matches the position of the 0-1 photoluminescence peak and is therefore assigned to stimulated emission from singlet excitons. The spectrum in the probe range below 2.1 eV reflects the singlet excited state absorption. All features in this system decay uniformly with a time constant of 11 ns, in good agreement with the mono-exponential photoluminescence decay discussed above for the same solution. No other excited state signatures are present within the resolution of the experiment. Taking into account the triplet absorption cross section and the noise level of the measurement, we set an upper limit of 6% as the yield of triplet excitons through intersystem crossing in this solution. We therefore conclude that in the dilute regime only singlet excitons are present.

We observe similar signatures immediately following photoexcitation of the concentrated solution (Figure 3b). The stimulated emission above 2.1 eV and shape of the photoinduced absorption band in the first 300 ps (blue lines) indicate that the initial photoexcited species is the same at both concentrations. The subsequent spectral evolution shows pronounced differences, however, as the initial singlet features evolve over several hundred picoseconds to form a new absorption profile (solid red trace) that was not observed in the dilute solution. This absorption profile displays a broad absorption feature in the visible probe region and sharper peaks in the near-IR. We attribute this intermediate transient absorption signal to the excimer formed from singlet excitons. It decays on the same timescale as the excimeric emission and is only present in concentrated solution. We observe that an increase in viscosity by the addition of polystyrene slows the formation of this species, indicating that it is formed via diffusional collisions (SI Appendix, Fig. S11 and S16). Analysis of the time constant of excimer formation and concentration reveals that the process follows second order reaction kinetics (Figure 4b and SI Appendix, Fig S11).

The excimer spectrum decays over nanoseconds to yield a third, sharply peaked absorption profile (Figure 3b, black trace). This final spectral signature has a 1.2  $\mu$ s lifetime and is assigned to triplet excitons, which we confirmed using a separate triplet sensitisation experiment. Briefly, in a degassed solution of *N*-methylfulleropyrrolidine and TIPS-tetracene we selectively excite the fullerene, which rapidly undergoes intersystem crossing to generate a large population of triplets. These are transferred to TIPS-tetracene through diffusional collisions (see SI Appendix, Figure S18-21), resulting in a long-lived signature that closely matches the features observed under direct excitation (Fig 4c, bottom)[26][27]. The remarkably sharp triplet absorption features we observe for the triplet exciton have been observed in a small set of other systems [18][28], where the rigidity of the molecule gives narrow absorption bandwidths, and are a distinct advantage of solution studies of acenes compared to the solid state. In this case, the sharp features allow us to distinguish the absorption signatures of the three species, and in particular track the evolution of the excimer to the triplet excitons. The sensitisation measurement also enabled a determination of the triplet absorption cross section of 5400  $\text{Lmol}^{-1}\text{cm}^{-3}$  at 1.63 eV, based on the degree of quenching of the triplet excitons on the sensitizer by TIPS-tetracene [27]. This value was used to obtain a triplet exciton yield of  $120\% \pm 20\%$  of the singlet exciton concentration. It is not surprising that the triplet exciton yield in this system is lower than in TIPS-pentacene solutions, considering the unfavourable energetics of singlet fission in TIPS-tetracene. This distinction notwithstanding, the high yield and observed concentration dependence of triplet exciton formation, analogous to TIPS-pentacene [18], confirm that the triplet excitons are produced in this system via diffusional singlet exciton fission.

#### Isolation of a Triplet-Character Intermediate

Following the identification of three separate species in concentrated TIPS-tetracene solution, we determine the time evolution of each using singular value decomposition and a spectral deconvolution code [29]. This code, based on a genetic algorithm, generates spectra that best reproduce the original transient absorption data while satisfying physical constraints such as spectral shape and population dynamics. The normalised population kinetics of singlet excitons, excimer and triplet excitons in the 300 mg/ml solution are presented in Figure 4(a). The singlet exciton population is shown from 100 fs, the peak of the instrument response, and decays with a 70 ps lifetime, in reasonable agreement with the fast PL decay observed with PL up-conversion (inset Fig. 1c). We observe excimer formation concomitant with the decay of the singlet exciton spectral features. The excimer population then decays with a time constant of 7.9 ns, consistent with the pho-

545 photoluminescence lifetime of 8.7 ns. The triplet exciton population  
546 rises with a 5 ns time constant and reaches a maximum between  
547 10-50 ns. Considering the short singlet lifetime and the extended  
548 lifetime of the excimer, we propose that triplet excitons arise  
549 directly from the excimer decay. We thus find that the excimer  
550 is in fact an intermediate in the endothermic formation of free  
551 triplet excitons. Interestingly, when we run the same analysis on  
552 the measurements of a TIPS-tetracene film at room temperature,  
553 we observe no distinct intermediate state: triplets appear to form  
554 directly from the initial state.

555 In addition to the evolution of the species over time, the  
556 distinct spectra of the singlet, excimer and triplet species were  
557 extracted in each spectral region. We are able to achieve such  
558 effective spectral and temporal resolution of these states due  
559 to the combination of diffusion-limited dynamics, the narrow  
560 absorption bands of triplet excitons in solution and the endothermicity  
561 of free triplet formation. As shown in Figure 4(c), the  
562 extracted spectra for the singlet and triplet excitons closely match  
563 reference measurements. The remaining spectrum, which can not  
564 be formed as a linear combination of the other two, is that of the  
565 excimer intermediate and reveals crucial information about the  
566 nature of that state.

567 We observe five sharp absorption features in the triplet exciton  
568 spectrum across the visible and NIR spectral regions (Figure  
569 3). The same absorption bands are present in the excimer spectrum  
570 and appear from 80 ps, when the process is still diffusion  
571 limited. These absorption bands of the excimer are sharp at low  
572 energies (1.28 and 1.46 eV) and appear on top of an underlying  
573 excited state absorption from 1.6- 2.2 eV. Notably, we observe  
574 that the triplet-like absorption bands of the excimer are shifted  
575 and broadened in energy from those of free triplet excitons by  
576 5-10 meV for each band (Figure 5). The five absorption bands  
577 simultaneously red-shift over the 1-5 ns timescale as the excimer  
578 population is replaced by free triplet excitons. The presence of  
579 triplet exciton absorption bands in the excimer indicates that it  
580 develops triplet character upon its formation, on a timescale too  
581 fast to be explained by intersystem crossing, which is clearly  
582 inefficient in the dilute solution. We propose that the shift observed  
583 in the triplet-pair state absorption reflects the subtle difference in  
584 the excited state manifolds of this state and free triplet excitons  
585 on isolated molecules.

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587 This result reveals a state that is electronically similar, yet not  
588 identical, to free triplet excitons that can be formed in < 100 ps  
589 from singlet excitons. This state and retains enough singlet  
590 character to re-form singlet excitons and itself luminesce. These  
591 observations - dual singlet-triplet character, showing the absorption  
592 of free molecular triplets at the same time as broader singlet-like  
593 bands - allow identification as a bound triplet-pair state <sup>1</sup>(TT). We  
594 consider that the formation of this state already constitutes the  
595 critical step of singlet exciton fission, though it is the subsequent  
596 dissociation into free triplet excitons that determines the final  
597 triplet yield. The subtle electronic structural differences that we  
598 uncover between the triplet-pair intermediate and free triplet  
599 excitons could give insight into the nature of triplet-pair states.  
600 In particular, the nature of coupling between two triplet excitons  
601 which appears to give a substantial stabilization, as we explain  
602 below, remains to be well understood.

#### 603 Endothermic Singlet Fission via a Triplet-Pair State

604 From these results we can put together the energetic picture  
605 of singlet fission in this endothermic system. It follows from the  
606 photoluminescence results above that the energy of the triplet-  
607 pair excimer state is equal to or slightly below that of the singlet  
608 exciton (2.3 eV). From analysis of the radiative and non-radiative  
609 decay rates for the singlet and excimer, and the concentration  
610 dependence, we determine that excimers are formed upon the  
611 collision of singlet excitons. In addition, the equilibrium between

612 the singlet and excimer manifolds strongly favours excimer for-  
613 mation, while loss via singlet emission represents a minor decay  
614 pathway for the excimer.

615 Our estimate of the endothermic barrier in this system is  
616 based on a triplet energy of 1.25 eV, the middle of the broad  
617 phosphorescence peak observed in thin films. We consider that  
618 an energy barrier of about 200 meV is consistent with activation  
619 over a thermal barrier. If we consider a Boltzmann distribution  
620 and the 5 ns time constant for free triplet formation, this system  
621 would require an attempt frequency on the order of 10<sup>11</sup>-10<sup>13</sup> Hz  
622 to overcome this energy barrier into independent triplet excitons.  
623 We conjecture that the reason such a slow thermal dissociation  
624 of the stabilised excimer intermediate into free triplets is able  
625 to proceed with such high efficiency is because competing decay  
626 channels are slower. Radiative decay via the singlet is substan-  
627 tially reduced in the concentrated solution as a result of forming  
628 excimers. The intrinsic radiative lifetime of 2 μs for the excimer is  
629 consistent with the microsecond radiative lifetimes reported for  
630 excimers of pyrene and anthracene [30][31], and gives sufficient  
631 time for competing non-radiative processes such as thermally  
632 activated triplet formation. These non-radiative decay processes  
633 shorten the excited state lifetime of the excimer to give the fluo-  
634 rescence lifetime of 8 ns that we measure in transient absorption  
635 and PL.

636 From the data available, it is difficult to ascertain the degree  
637 to which the two-step mechanism of fission in solution relates  
638 to the solid state. Although we observe no distinct intermediate  
639 in films of TIPS-tetracene, it is possible, for instance, that the  
640 conformational constraints of the film prevent any significant  
641 stabilization of the intermediate state that would measurably  
642 distort its absorption spectrum relative to free triplets. Without  
643 a clear identification of such effects, though, the mechanism of  
644 this endothermic singlet fission will remain in question. We note,  
645 however, that it would be surprising for the same material to be  
646 capable of singlet fission via two completely distinct mechanisms  
647 and propose that a strongly stabilized TT intermediate still plays  
648 an important role.

649 We can compare the results here with studies from films of  
650 tetracene, where the first step of highly efficient endothermic  
651 singlet fission is temperature independent [22][23] and has been  
652 proposed to involve barrier-free formation of an intermediate  
653 state [32][33] or tunnelling into a bound triplet pair [4]. We  
654 find that our model is in qualitative agreement with these other  
655 studies; our endothermic system reveals rapid formation of a  
656 bound intermediate with triplet character that goes on to produce  
657 two free triplet excitons over a longer timescale. We speculate that  
658 the stabilization we observe in the triplet-pair excimer, relative to  
659 free triplet excitons, may occur to a lesser degree in the solid state  
660 as well and enable the fast formation of bound triplets.

661 These results provide an important and surprising insight into  
662 the nature of the triplet-pair state, which has long played a central  
663 role in theories of singlet fission but never been directly observed.  
664 The bound state can be significantly stabilized relative to two free  
665 triplet excitons, here by 100-300 meV, indicating a substantial  
666 interaction between the triplets. A similar effect is observed  
667 in some polyene-type systems, in which the doubly-excited 2A<sub>g</sub>  
668 state can be identified as a bound triplet pair [34]. In poly(3-  
669 dodecylthiénylenevinylene), for instance, the 2A<sub>g</sub> state is substan-  
670 tially lower in energy than the threshold for singlet exciton fission,  
671 and indeed offers a rapid decay channel for triplet pairs [25].  
672 Multi-exciton states with A<sub>g</sub> symmetry have also been invoked  
673 to explain fission in calculations of crystalline pentacene, though  
674 in that system there is no evidence of any significant energetic  
675 stabilization in this state [35]. It is possible that stabilized triplet-  
676 pair states akin to the one presented here play an important role  
677 in fission across different molecular systems, especially nominally  
678 endothermic materials such as tetracene, but more exploration of  
679  
680

this phenomenon is needed. In this TIPS-tetracene system, the stabilization we observe and the accompanying effects of this coupling on the transient absorption spectra, should provide fertile ground for advanced theoretical investigations of the interactions between adjacent triplet excitons. Explorations of the nature and electronic structure of this triplet-pair intermediate via multi-pulse techniques will enable a more complete understanding of the mechanism of singlet fission and may establish the importance of such stabilized states for mediating triplet formation in endothermic systems.

## Materials and Methods

TIPS-tetracene was synthesised according to the procedure in reference [37].

For most of the photophysical characterisation (see SI appendix for details) TIPS-tetracene was measured in solutions of chloroform (3-300 mg/ml) in sealed 1 mm pathlength cuvettes. Steady state UV-Vis absorption

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spectra were taken at RT using a Cary 400 UV-Visible Spectrometer. For these measurements 200  $\mu\text{m}$  and 5  $\mu\text{m}$  pathlength cells were used. Steady state and time-resolved fluorescence spectra were acquired with a PicoQuant LDH400 pulsed laser and SpectroPro2500i spectrograph. Photoluminescence up-conversion was measured using a Jobin Yvon:Triax90 spectrometer and Jobin Yvon:Symphony CCD.

Femtosecond and nanosecond transient absorption measurements were carried out with an amplified Ti:Sapphire (Spectra Physics Solstice) laser system and imaged using an Andor Shamrock SR 303i spectrometer. See SI Appendix for more details regarding the TA set-up and data analysis techniques.

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